

P08.10.110*Acta Cryst.* (2008). A64, C452**New $M_{1/3}Re_{2/3}O_2$ (M = Fe, Co, Ni) oxides with rutile-like structures**Daria A. Mikhailova^{1,2}, Helmut Ehrenberg¹, Gerhard Brey³, Hartmut Fuess²

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For the system $M_{1/3}Re_{2/3}O_2$ (M = Fe, Co, Ni) different rutile or rutile-derived structural modifications were found depending on the temperature during high-pressure high-temperature syntheses. The crystal structures have been determined by single crystal X-ray diffraction. For synthesis temperature higher than 1300 °C, phases with tetragonal rutile aristotype structure (S. G. $P4_2/mnm$) and a statistical distribution of M- and Re-atoms on the metal site in the structure were obtained. At lower synthesis temperature, rutile-like structures with orthorhombic or monoclinic symmetry, partial order on M- and Re-sites and metallic Re-Re bonds were observed for $Co_{1/3}Re_{2/3}O_2$ and $Ni_{1/3}Re_{2/3}O_2$. A monoclinic $CrWO_4$ -type structure (S. G. $C2/m$) with only Re-atoms on the 4g site and statistically distributed Ni- and Re-atoms on the 4i site was adopted by $Ni_{1/3}Re_{2/3}O_2$. Single crystals $Co_{1/3}Re_{2/3}O_2$ with orthorhombic $CrWO_4$ -type structure (S. G. $F222$) and also partially mixed Co, Re-positions were found together with a monoclinic modification, which is isotypic to monoclinic $Ni_{1/3}Re_{2/3}O_2$. Note, that another orthorhombic modification (S. G. $Cmmm$) was reported for the composition $Co_{1/2}Re_{1/2}O_2$ with distinct positions of Co and Re and without any metallic Re-Re-bond [1]. Unfortunately, the synthesis conditions were not described in sufficient detail to allow a comparison with our preparation method. $Ni_{1/3}Re_{2/3}O_2$ with the rutile-structure orders ferro- or ferrimagnetically at 23.5 K, whereas tetragonal $Co_{1/3}Re_{2/3}O_2$ shows two magnetic transitions: below 17.5 K the ferromagnetic component dominates in contrast to an antiferromagnetic order between 27.0 and 17.5 K.

[1] W. H. Baur, W. Joswig, G. Pieper, D. Kassner, J. Solid State Chem. 99 (1992) 207-211.

Keywords: high-pressure high-temperature synthesis, rutile-like structure, metallic Re-Re bond

P08.10.111*Acta Cryst.* (2008). A64, C452**Compression and thermal behavior of GeO_2 glass**

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One fascinating high-pressure behavior of tetrahedral glasses and melts is the local coordination change with increasing pressure, which provides a structural basis for understanding numerous anomalies in their high-pressure properties. Because the coordination change is often not retained upon decompression, studies must be conducted in situ. Previous in situ studies have revealed that the short-range order of tetrahedrally structured glasses and melts changes above a threshold pressure and gradually transforms to an octahedral form with further pressure increase. We report compression behavior of GeO_2 glass up to 35 GPa, and a thermal effect associated with the coordination change at given pressures.

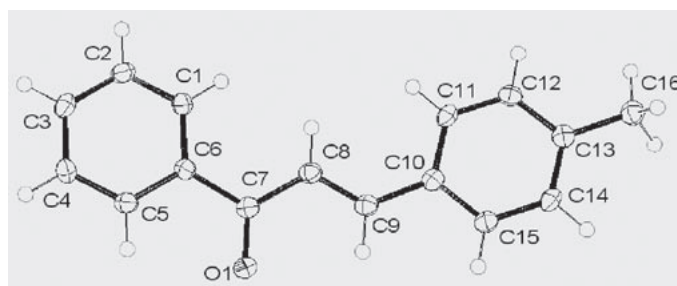
The results show a clear anomaly in compression curve associated with the coordination change, as well as distinct thermal behaviors of GeO_2 glass in tetrahedral, octahedral, and their intermediate forms. An unusual thermally induced densification, as large as 16%, was observed on a GeO_2 glass at a pressure of 5.5 GPa. The large thermal densification at high pressure was found to be associated with the 4- to 6-fold coordination increase. Experiments at other pressures show that the tetrahedral GeO_2 glass displayed small thermal densification at 3.3 GPa arising from the relaxation of intermediate range structure, whereas the octahedral glass at 12.3 GPa did not display any detectable thermal effects.

Keywords: high pressure, coordination change, compression

P08.10.112*Acta Cryst.* (2008). A64, C452**Disappearing and reappearing polymorphism in *p*-methylchalcone**Inna Barsky¹, Bernstein Joel¹, Peter W Stephens², Kevin H Stone², Eugene Cheung³, Magali B Hickey³

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The polymorphism of *p*-methylchalcone (*p*-MC) has been the subject of interest for about 80 years. One stable form (Form I) and two metastable forms (Form II and Form IV) of *p*-methylchalcone have been obtained, with Form II having previously been reported to be a disappearing polymorph. To prevent the conversion of Form II, which has a melting point of 89-91 °C, into the stable form it was produced in conditions free from seeds of the stable form. Form IV was discovered serendipitously as a single crystal that appeared in the preparation of a powder of Form II. Forms I and II have also been characterized by optical microscopy, differential scanning calorimetry (DSC), variable temperature powder X-ray diffraction and spectroscopic analysis. The crystal structures of these three forms have been solved, Forms I and IV by single-crystal methods and Form II from synchrotron powder diffraction.



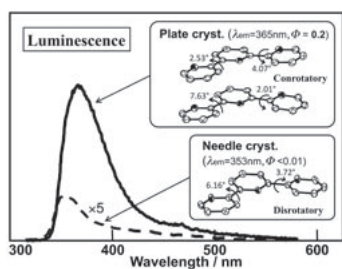
Keywords: *p*-Methylchalcone, polymorphism, X-ray structure determination

P08.11.113*Acta Cryst.* (2008). A64, C452-453**Switchable polymorph-dependent luminescence of terpyridine**Toshiki Mutai¹, Yasuhiro Shigemitsu², Hirohiko Houjou¹, Koji Araki¹

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2,2':6',2''-Terpyridine (tpy), which is practically non-fluorescent ($\Phi < 0.01$) in organic solutions, in an amorphous solid and a needle crystal ($P2_12_12_1$, $Z=4$), was found to show an efficient solid-state luminescence (365 nm, $\Phi = 0.2$) upon formation of a plate crystal ($P2_1/c$, $Z=8$). Furthermore, effective on-off switching of this solid-state luminescence was realized by heat-mode interconversion between the plate and needle crystals. It was shown that the rate constant of the non-radiative relaxation of the needle crystal ($k=1.2 \times 10^9 \text{ s}^{-1}$) was an order of magnitude larger than the plate crystal, while that of the emissive process were comparable ($k \sim 10^7 \text{ s}^{-1}$). In contrast to a frozen solution, both polymorphs did not exhibit phosphorescence at 77 K, suggesting that the triplet state might not be involved in the non-radiative process. Comparing both polymorphs, tpy molecules were in different conformation, conrotated and disrotated, which might be due to a different molecular packing. Relation between the difference in the crystal structure and the solid-state luminescence property was further studied.



Keywords: luminescence, polymorphism, heterocyclic compounds

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Polymorphism of chlorpropamide: Structure and transitions

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The importance of the polymorphism of drugs can hardly be overestimated. Detailed structural studies not only allow to identify a selected form reliably, but also provide a valuable insight into the structure-properties relations, especially, when combined with vibrational spectroscopy, thermal analysis and calorimetry. Chlorpropamide an antidiabetic drug, has been known to be highly polymorphic since a very long time, but the crystal structures of all the claimed forms but the one produced commercially remained unsolved. Structure of only one polymorph was known when we started our investigation. We solved three new ones. The molecule is very flexible and different parts of the molecule can freely rotate and bend. Having crystal structure data, we defined quantitatively the values of torsion angles and variations in hydrogen bonds among them. Motif of hydrogen bonds is really the same, and the polymorphism results mainly from the difference in intramolecular (conformational polymorphism). Packing of neighbouring molecules in the structure is similar for all polymorphs but one (beta). Hydrogen bonds in that polymorph differ from those in the rest ones. We investigated polymorph transitions near the melting point by using DSC, IR

spectroscopy, and X-ray powder diffraction. All the polymorphs are proved to transform into the fifth polymorph, epsilon, which melts then. Kinetics of polymorph transition is inhibited for beta polymorph. This work was supported by the grants from BRHE (RUX0-008-NO-06/BP2M08, Y3-C-08-01), Innovation Project "Education" from the Russian Ministry of Education and Science #456, and Integration Projects #49 and #110 of SB RAS.

Keywords: polymorphism, drug structures, hydrogen bonds

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Structure formation effects on electro-optics of montmorillonite clay-5CB liquid crystal composites

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Nanomaterials based on liquid crystals (LCs) and montmorillonite (MMT) clay are perspective due to their applications in the information record and storage devices, etc. The nematic LC, pentylcyanobiphenyl (5CB) was used in our composites. The MMT was modified with octadecylbenzyltrimethylammonium chloride (OBDM) and dioctadecyltrimethylammonium chloride (DODM), which leads to the better chemical affinity of the clay to LCs and increase of MMT basal spacings for the penetration of 5CB dimers to the interlayer space. The nature of the surfactant is responsible for chemical affinity between the clay and LC, affecting the structure formation in the composites. These properties explain their different electro-optical (EO) characteristics. In the case of OBDM-MMT, well separated small clay particles are uniformly distributed in the 5CB medium. Under applied electric field, this mobile system is easily oriented along the field direction resulting in significant increase in optical transparency, when the applied voltage increases. Due to the fairly strong molecular interactions between the composite components, the field-induced alignment of 5CB domains remains the same even when the electric field is removed (considerable EO memory). Contrary, due to the smaller affinity of DODM to 5CB molecules, DODM-MMT particles are only partially covered by LC layer, which allows them to aggregate. These aggregates form a stable colloidal network with 5CB dimers. In EO measurements, when an electric field is applied to the composite, its transparency increases, but less, than for the former one. So the EO memory of the composite with DODM-MMT is low, but the contrast is high. These investigations will assist in the development of the composites with desired optical characteristics.

Keywords: LC-clay composites, X-ray diffraction, electro-optical properties

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Crystal structure of metastable cubic B₁-phase of the La₂Mo₂O₉ single crystal

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